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SOVIET EXPERIMENTAL DATA ON ALKOXYISOPROPYL ESTERS OF PHOSPHOROUS ACID AND THEIR PROPERTIES

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The work on organic phosphorus compounds which is being done at the Laboratory of Organic Chemistry of Kazan State University leads to or approaches the synthesis of nerve poisons, as can be seen from the constitution of the compounds mentioned in this paper and in earlier reports of work done at that laboratory. The reactions listed and described in the series of reports in question are definitely of interest from that standpoint, both for the synthesis of compounds which must be assumed to have toxic properties, e.g., nerve poisons and others, and considered within that general field of research, i.e., leading to other compounds which have more pronounced or more specific toxic properties, or are perhaps more volatile and stable.

Introduction

A preceding report (1) described tri-beta-methoxy- and tri-beta-ethoxyethyl esters of phosphorous acid. These alkoxyethyl esters of phosphorous acid, through the action of corresponding halogen-substituted simple ethers, underwent isomerization and were converted into di-beta-methoxy- and di-beta-ethoxyethyl esters of beta-alkoxyethylphosphonic acids. These esters also reacted with bromomethyl ethers to give di-beta-methoxy- and di-beta-ethoxyethyl esters of alkoxymethylphosphonic acids.

For this paper, propyleneglycol primary monethyl ether and propyleneglycol primary monoisopropyl ether were used as starting materials. They were prepared by the addition of alcohol to propylene oxide in the presence of NaOH in conformity with the work of Chitwood and Freure (2).

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Tri-beta-ethoxy- and tri-beta-isopropyloxyisopropyl esters of phosphorous acid were prepared according to the method of Milobedzki and Sachnovski (3), as modified by Ye. N. Nikolayeva by reacting phosphorus trichloride with the corresponding primary ethers of propyleneglycol in the presence of freshly distilled dimethylaniline in absolute dry ether. This reaction can be expressed by the equation:

$$3CH_3\text{-}\underset{\underset{OH}{|}}{CH}\text{-}CH_2OR + PCl_3 + 3C_6H_5N(CH_3)_2 = \left(\begin{matrix}CH_3\\ ROCH_2\end{matrix}\!\!>\!CHO\right)_3P + 3C_6H_5N(CH_3)_2 \cdot HCl,$$

where R represents an ethyl or an isopropyl radical.

Tri-beta-ethoxy- and tri-beta-isopropyloxyisopropyl esters of phosphorous acid are colorless mobile liquids with a weak odor resembling that of phosphites. These esters react with cuprous iodide with a temperature increase of from 20 to 41 degrees, but it was not possible to obtain crystalline products even after prolonged standing.

The latter ester, reacted with ethyl-beta-bromoethypropyl ether, was isomerized into the di-beta-ethoxyisopropyl ester of beta-ethoxyisopropylphosphonic acid. (A. Ye. Arbuzov earlier described the isomerization of the esters of phosphorous acid in detail.)

Tri-beta-ethoxyisopropyl ester of phosphorous acid was reacted with simple halogensubstituted ethers to form esters of alkoxymethylphosphonic acids.

Abramov and his collaborator in this study investigated the action of monobromomethyl, bromomethylethyl, bromomethylpropyl, and chloromethylbutyl ethers on tri-beta-ethoxyisopropyl ester of phosphorous acid.

The isomerization and reaction of simple halogen-substituted ethers on this ester can be expressed as follows:

$$\left(\begin{matrix}CH_3\\ C_2H_5OCH_2\end{matrix}\!\!>\!CHO\right)_3P + BrCH_2OR = \left(\begin{matrix}CH_3\\ C_2H_5OCH_2\end{matrix}\!\!>\!CHO\right)_3P\!\!<\!\!\begin{matrix}CH_2OR\\ Br\end{matrix}$$

$$\begin{matrix}CH_3\\ C_2H_5OCH_2\end{matrix}\!\!>\!CHO \quad 2 \quad P\!\!<\!\!\begin{matrix}CH_2OR\\ \boxed{\begin{matrix}CH_3\\ C_2H_5OCH_2\end{matrix}\!\!>\!CH\,O\,P\!<\!Br}\end{matrix} = \left(\begin{matrix}CH_3\\ C_2H_5OCH_2\end{matrix}\!\!>\!CHO\right)_2 P\!\!<\!\!\begin{matrix}CH_2OR\\ O\end{matrix} + C_2H_5OCH_2CHBrCH_3.$$

The di-beta-ethoxyisopropyl esters of alkoxymethylphosphonic acids thus obtained are colorless, odorless liquids.

The authors attempted to prepare tri-beta-phenoxyethyl ester of phosphorous acid from ethyleneglycol monophenyl ether and phosphorus trichloride in the presence of freshly distilled dimethylaniline, but could only assume that it had been formed in the reaction, which proceeded with the liberation of the chloride of dimethylaniline, since they were unable to liberate this compound by distillation in vacuum. Violently increasing decomposition occurred during the distillation, and some of the substance was distilled off. The residue in the flask was converted into a thick viscous mass with an orange color, apparently traceable to liberated phosphorus. The distilled substance partially crystallized in colorless crystals which were identified as phenol through the odor, the violet color reaction with ferric chloride, and by the preparation of tribromophenol with melting point 94 degrees. The liquid part interacted with cupric iodide, giving a temperature increase of from 25 to 35 degrees, a

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fact which indicated specifically the presence of tri-beta-phenoxyethyl ester of phosphorous acid and in general indicates the presence of compounds of trivalent phosphorus. The liquid was again distilled, and once more underwent decomposition. Apparently separation of phenol with formation of vinyl ester of phosphorous acid or of mixed vinyl-beta-phenoxyethyl ester of this acid occurs, followed by polymerization of the esters. The reaction proceeds according to the equation:

$$(C_6H_5OCH_2CH_2O)_3P \rightarrow C_6H_5OH + (CH_2=CHO)_3P \text{ or } CH_2=CHOP(OCH_2CH_2OC_6H_5)_2.$$

The action of phosphorous trichloride on the propyleneglycol primary monethyl ether resulted in the formation of di-beta-ethoxyisopropylphosphorous acid according to the equation:

$$3C_2H_5OCH_2\overset{CH_3}{\underset{}{>}}CHOH + PCl_3 = \left(C_2H_5OCH_2\overset{CH_3}{\underset{}{>}}CHO\right)_2 POH + C_2H_5OCH_2CHClCH_3 + 2HCl.$$

This acid is a colorless, odorless liquid.

The action of phosphorus trichloride on ethyleneglycol phenyl ether produced di-beta-phenoxyethylphosphorous acid:

$$3C_6H_5OCH_2CH_2OH + PCl_3 = (C_6H_5OCH_2CH_2O)_2POH + C_6H_5OCH_2CH_2Cl + 2HCl.$$

As a result of distillation of the products of the reaction, a fraction corresponding, according to published data, to beta-chloroethylphenyl ester was obtained with a 100 percent yield. Formation of this compound confirms that the reaction proceeds according to the above equation.

The residue, which evidently consists of di-beta-phenoxyethylphosphorous acid, apparently decomposed as a result of distillation in vacuum, just as the tri-ester does. The distilled fraction corresponded to phenol, as confirmed by the odor, the violet color reaction with ferric chloride, and by preparation of tribromophenol with melting point 94 degrees. There remained in the flask a thick orange mass, probably consisting of a polymer of divinyl-/or monovinylphosphorous acid:

$$(C_6H_5OCH_2CH_2O)_2POH \rightarrow C_6H_5OH + (CH_2=CHO)_2POH \text{ or } CH_2=CHO\text{-}\underset{\underset{O}{\|}}{P}\text{-}OCH_2CH_2O\text{-}C_6H_5 \quad (H)$$

An attempt to prepare the silver salt from damp di-beta-phenoxyethylphosphorous acid was not successful.

As a result of the reaction of phosphorous trichloride on ethyleneglycol phenyl ether, according to N. A. Menshutkin (4), the chloride of phenoxyethylphosphorous acid -- a colorless liquid, fuming in the air -- was obtained.

Experimental Part

1. Preparation of Tri-beta-ethoxyisopropyl Ester of Phosphorous Acid.

This compound was prepared from propyleneglycol primary monethyl ether which had previously been obtained from absolute alcohol and propylene oxide in the presence of caustic soda (2); after two consecutive distillations in the column with a glass adapter, a fraction with boiling point 130-131 degrees, n_D^{20} 1.4054, d_4^{20} 0.894, was obtained.

Into a round-bottomed flask equipped with a reflux condenser, a drop funnel, and an agitator, were placed 90 grams of the propyleneglycol primary monoethyl ether, 105 grams of freshly distilled dimethylaniline, and 300 milliliters of dry ether. To this mixture, during cooling with snow and under vigorous stirring, were gradually added from the drop funnel 39 grams of PCl_3. Stirring was continued for a half hour. The precipitated dimethylaniline chloride was filtered off and washed with dry ether. The ethyl ether was distilled on a water bath, and the residue was then distilled in vacuum. After two consecutive distillations, a fraction with boiling point 156-158 degrees at 9 millimeters was obtained. Yield: 68 grams or 70 percent of the theoretical.

n_D^{20} 1.4320; d_4^{20} 0.983; MR_D 89.4; $C_{15}H_{33}O_6P$. Calculated MR_D 89.5.

0.2792 g of substance weighed in; 31.7 ml NaOH (T 0.2843)

(cf. Neumann Z. physiol, XXXVII, 129, 1902; XLIII, 35, 1904; 1 ml of this solution contains 0.000786 g P.)

0.1656 g of substance weighed in; 19.4 ml NaOH (T 0.2843)

Found % of P: 8.93; 9.05

Calculated % of P: 9.11

$C_{15}H_{33}O_6P$.

2. Action of Cupric Iodide on Tri-beta-ethoxyisopropyl Ester of Phosphorous Acid

A known quantity of cupric iodide was added all at once to 2 grams of the ester in a test tube; this produced an exothermic reaction in which the temperature of the reacting substances increased from 19 to 41 degrees. Then the tube was heated until the iodide had almost completely dissolved. The products of the reaction were treated with water to remove the cupric iodide and were then extracted with ether. When the ether was evaporated, a syrupy transparent liquid remained. It did not crystallize after prolonged standing.

3. Isomerization of Tri-beta-ethoxyisopropyl Ester of Phosphorous Acid By the Action of Ethyl-beta-bromopropyl Ether

5.3 grams of the ester and 0.65 grams of the ether were sealed in a tube provided with a constriction to permit better observation of the volume change (see Dissertation, A. Ye. Arbuzov, 1914). This tube was heated at 120 degrees for 9 hours with no volume change. The contents of the tube were distilled in vacuum. Two consecutive distillations produced a fraction with boiling point 152-164 degrees.

n_D^{20} 1.4320; d_4^{20} 1.012; MR_D 87.14; $C_{15}H_{33}O_6P$. Calculated MR_D 86.17

4. Preparation of Ethyl-beta-bromopropyl Ether

Into a flask equipped with a reflux condenser and containing 15 grams of propyleneglycol monethyl ether were cautiously poured 13 grams of phosphorous tribromide. The flask was then heated on an oil bath, and the reaction products were distilled in vacuum. Two consecutive distillations gave 11 grams of a fraction with boiling point 32-34 degrees at 10 millimeters.

n_D^{20} 1.4410; d_4^{10} 1.243; MR_D 35.26; $C_5H_{11}OBr$. Calculated MR_D 34.7

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5. Action of Monobromomethyl Ether on Tri-beta-ethoxyisopropyl Ester of Phosphorous Acid

Reactions in which halogen-substituted ethers acted on tri-beta-ethoxyisopropyl ester of phosphorous acid were carried out in a round-bottomed flask equipped with a reflux condenser and a drop funnel. In this particular exothermic reaction, 3.7 grams of the ether were gradually added to 10 grams of the ester. Upon completion of the reaction, the resulting mass was heated on an oil bath at 120 degrees for 1-2 hours. Products of the reaction were distilled in vacuum. After two consecutive distillations 4.8 grams of a fraction with boiling point 165-168 degrees at 16 millimeters were separated.

n_D^{20} 1.4272; d_4^{20} 1.049; MR_D 72.71; $C_{12}H_{27}O_6P$. Calculated MR_D 72.90

0.1744 g of substance weighed in; 23.4 ml NaOH (T 0.02843)

0.1208 g of substance weighed in; 17.1 ml NaOH (T 0.02843)

Found % of P: 10.5; 10.3

Calculated % of P: 10.39

$C_{12}H_{27}O_6P$

6. Action of Bromomethylethyl Ether on Tri-beta-ethoxyisopropyl Ester of Phosphorous Acid

To 10 grams of the ester 4 grams of the ether were gradually added. After heating, the reaction product was distilled in vacuum, and 3.9 grams of a fraction with boiling point 164-166 degrees at 7 millimeters were obtained.

n_D^{20} 1.4312; d_4^{20} 1.040; MR_D 77.45; $C_{13}H_{29}O_6P$. Calculated MR_D 77.52

0.1201 g of substance weighed in; 15.6 ml NaOH (T 0.02843)

0.1234 g of substance weighed in; 16.0 ml NaOH (T 0.02843)

Found % of P: 10.2; 10.11

Calculated % of P: 9.9

$C_{13}H_{29}O_6P$

7. Action of Bromomethylpropyl Ether on Tri-beta-ethoxyisopropyl Ester of Phosphorous Acid

To 7 grams of the ester 3.1 grams of the ether were added, and after two consecutive distillations, the reaction product yielded 4.5 grams of a fraction with boiling point 158-160 degrees at 6 millimeters.

n_D^{20} 1.4310; d_4^{20} 1.029; MR_D 82.02; $C_{14}H_{31}O_6P$. Calculated MR_D 82.14

0.1018 g of substance weighed in; 11.7 ml NaOH (T 0.02843)

0.1380 g of substance weighed in; 15.8 ml NaOH (T 0.02843)

Found % of P: 9.02, 8.99

Calculated % of P: 9.5

$C_{14}H_{31}O_6P$

8. Action of Chloromethylbutyl Ether on Tri-beta-ethoxyisopropyl Ester of Phosphorous Acid

To 7 grams of the ester 2.5 grams of the ether were gradually added and the reaction product was heated on an oil bath and then distilled in vacuum. After two consecutive distillations 4.8 grams of a fraction with boiling point 210-213 degrees at 35 millimeters were obtained.

n_D^{20} 1.4309; d_4^{20} 1.013; MR_D 86.62; $C_{15}H_{33}O_6P$. Calculated MR_D 86.76

0.1170 g of substance weighed in; 11.6 ml NaOH (T 0.02843)

0.1714 g of substance weighed in; 12.1 ml NaOH (T 0.02843)

Found % of P: 7.8; 7.98

Calculated % of P: 8.1

$C_{15}H_{33}O_6P$.

9. Preparation of Tri-beta-isopropoxyisopropyl Ester of Phosphorous Acid

Propyleneglycol primary isopropyl ether was prepared from isopropyl alcohol and propylene oxide in the presence of caustic soda (2). Distillation was conducted in a column with a glass adapter and a fraction with boiling point 137-138 degrees collected. Its constants were found to be n_D^{20} 1.4070, d_4^{20} 0.879, in conformity with data from literature.

Preparation of this ester was carried out in analogous fashion to the preparation of tri-beta-ethoxyisopropyl ester of phosphorous acid. In the reaction, 50 grams of the primary ether, 51.2 grams of freshly distilled dimethylaniline, and 150 milliliter of dry ether were used. To this mixture during cooling and vigorous stirring were added 19.4 grams of PCl_3. After separation from dimethylaniline hydrochloride and distillation of the ether, the remaining reaction product was distilled in a vacuum to obtain 18 grams of a fraction with boiling point 160-168 degrees at 12 millimeters. This was not a pure product. In a second experiment 13 grams of an analogous fraction were prepared. The total of 31 grams from both experiments was then treated with sodium metal to remove acid esters. The tri-ester was finally obtained by fractional distillation. Boiling point was 152-155 degrees at 10 millimeters.

n_D^{20} 1.4300; d_4^{20} 0.9515; MR_D 103.6; $C_{18}H_{39}O_6P$. Calculated MR_D 103.37

0.1220 g of substance weighed in; 12.8 ml NaOH (T 0.02843)

0.1032 g of substance weighed in; 10.6 ml NaOH (T 0.02843)

Found % of P: 8.24; 8.07

Calculated % of P: 8.1

$C_{18}H_{39}O_6P$

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10. Preparation of Tri-beta-phenoxyethyl Ester of Phosphorous Acid

Ethyleneglycol phenyl ether was prepared from commercial chlorohydrin and sodium phenolate by prolonged boiling. For these syntheses a fraction with boiling point 118-121 degrees at 15 millimeters was taken. In this experiment 200 grams of the ether, 164 grams of freshly distilled dimethylaniline, and 500 milliliters of dry ether were used. To this mixture, under cooling and mixing, were added 62.2 grams of PCl_3. The dimethylaniline hydrochloride was then filtered off and the reaction product distilled in vacuum. This distillation proceeded with a gradual but constant decomposition. Along with this decomposition, the ester was partially distilled away. The residue in the flask was a thick orange mass. Repeated distillation of the fraction gave an analogous result. The distilled product crystallized in the condenser and was found to be phenol. It gave a violet color reaction with ferric chloride, and as a result of bromination was converted into tribromophenol with melting point 94 degrees. A mixed specimen did not give a melting point depression. The various fractions reacted with curpic iodide in an exothermic reaction. The maximum temperature increase with one of the fractions was from 25 to 35 degrees.

11. Preparation of Di-beta-ethoxyisopropylphosphorous Acid

To 80 grams of propyleneglycol primary ethyl ether during stirring and cooling were gradually added 35.2 grams of PCl_3. The HCl which formed was later blown off with dry air. The reaction product was then distilled in vacuum, and three consecutive distillations gave 25 grams of a fraction with boiling point 135-137 degrees at 9 millimeters.

n_D^{20} 1.4270; d_4^{20} 1.049; MR_D 62.4; $C_{10}H_{23}O_5P$. Calculated MR_D 61.34

0.1562 g of substance weighed in; 24.3 ml NaOH (T 0.02843)

0.2710 g of substance weighed in; 43.0 ml NaOH (T 0.02843)

Found % of P: 12.24; 12.46

Calculated % of P: 12.20

$C_{10}H_{23}O_5P$

12. Preparation of Di-beta-phenoxyethylphosphorous Acid

To 100 grams of ethyleneglycol monophenyl ether were added 33.2 grams of PCl_3. The HCl was removed as in the previous experiment, and the reaction product distilled in vacuum. A fraction with boiling point 90-93 degrees at 4 millimeters was obtained.

n_D^{20} 1.5258; d_4^{20} 1.121; MR_D 42.47; $C_8H_9OCl = 3$. Calculated MR_D 42.05

These constants check with the published data for beta-chloroethylphenyl ether. Yield: 40 grams or 100 percent of the theoretical. Under continuous distillation the residue underwent constant, gradual decomposition. The distilled product partially crystallized, and was found to be phenol: with ferric chloride it gave a violet color reaction, and was brominated to form tribromophenol with melting point 94 degrees.

The residue was a viscous orange mass.

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An attempt to prepare the silver salt from the residue after distilling off the beta-chloroethylphenyl ether (in a separate experiment) did not give positive results. The salt was prepared by pouring a solution of silver nitrate into a water solution of the residue with a small quantity of ammonia. The deposited silver quickly darkened the residue.

13. Preparation of the Chloride of Beta-phenoxyethylphosphorous Acid

This compound was prepared, according to N. A. Menshutkin (4), by adding 45 grams of ethyleneglycol monophenyl ether to 44.8 grams of PCl_3 while stirring. The HCl was blown off with dry air and the residue distilled. Two consecutive fractional distillations produced 24 grams of a fraction with boiling point 150-152 degrees at 9 millimeters.

n_D^{20} 1.5437; d_4^{20} 1.328; MR_D 56.71; $C_8H_9O_2Cl_2P = 3$. Calculated MR_D 56.75

0.1040 g of weighed in substance; 16.8 ml NaOH (T 0.02181)

0.0986 g of weighed in substance; 16.6 ml NaOH (T 0.02181)

Found % of P: 12.7; 13.03

Calculated % of P: 12.97

$C_8H_9O_2Cl_2P$

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